TOWARDS SUSTAINABLE ALUMINA PRODUCTION

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ABSTRACT:

This paper, an overview of research pursued at NML towards sustainable alumina production, deals with: (a) a chemical beneficiation of red mud to recover all its constituents, and (b) a novel process to reduce the alumina and soda content of red mud using mechanochemical activation (MA) of bauxite. As a part of the study on chemical beneficiation of red mud, phase stability in the system Fe_2O_3-Al_2O_3-Na_2CO_3-C has been investigated using free energy minimization. Using these results, a process involving solid-state carbothermic reduction of red mud in the presence of soda, water leaching for alumina recovery and magnetic separation of leach residue for the separation of iron and TiO_2 rich fraction has been evaluated. Experimental results are explained using extensive X-ray diffraction and SEM-EDS studies on various solid residues generated in the different stages of the process. Mechanical activation of bauxite is investigated: (a) as pre-treatment to the Bayer process; and (b) mechanochemical leaching of bauxite, i.e. simultaneous milling and leaching of bauxite. The superiority of mechanochemical leaching over the existing Bayer process practice and MA as pretreatment has been established. Using the novel process the approach of mechanochemical leaching, reduction in soda content of red mud to less than 1% and alumina content to less than half is possible with additional benefits in terms of moderation in process condition, simplicity of the process and efficient utilization of energy. Merits of the investigated processes have been highlighted vis-à-vis previous studies on red mud utilization and minimization of its environmental impact.

INTRODUCTION :

Red mud or bauxite tailings produced during alkali leaching of bauxite by the Bayer process have continued to be one of the prime concerns of aluminium/alumina industry from the point of view of resource conservation and protection of environment. For every tonne of alumina produced, 1-1.5 tonnes of red mud is generated as a waste. It is estimated that nearly 100 million tonnes of red mud is produced annually worldwide, and presently in India alone 3-4 million tonnes red mud is generated. Red mud may contain as much as 63% Fe_2O_3, 23% Al_2O_3, 4% Na_2O and 24% TiO_2 depending upon chemistry and mineralogy of bauxite and bauxite treatment technology. Large number of attempts has been made to find metallurgical as well as non-metallurgical applications. Most metallurgical attempts failed due to availability of rich natural resources (e.g. for Fe and TiO_2) and unfavorable economics. Non-metallurgical applications could consume only a small fraction of red mud generated. While best available technologies (BAT) are in practice for red mud disposal, the utilization of red mud and minimization of its soda and alumina content are of great significance from the point of view of resource conservation and sustainability of the alumina/aluminium production. This paper deals with studies at National Metallurgical Laboratory (NML) on chemical beneficiation of red mud to recover all its constituents. In addition, a novel process developed in the Laboratory to reduce the alumina and soda content of red mud using mechanochemical activation (MA) of bauxite is described as step towards sustainable Bayer process.

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CHEMICAL BENEFICIATION OF RED MUD

The studies on chemical beneficiation of red mud [1,2] were prompted at NML by a process that was originally developed for the removal of alumina from aluminous iron ores [3]. The major steps involved in the process are roasting of a mix consisting of red mud, soda and carbon, leaching of the roasted mass to recover alumina and magnetic separation of the leach residue. The iron rich magnetic fraction is smelted to obtain pig iron or any other iron alloy, and non-magnetic fraction is utilized for the recovery of minor constituents, such as TiO_2. Unlike apparently similar Soda (or Soda-Lime)-Carbon sinter process for red mud [4,5], roasting is carried out at a lower temperature such that sintering or fusion is avoided. The process is claimed to offer several advantages; for example, almost complete recovery of alumina, high purity of magnetic fraction resulting in considerable savings of flux and energy during smelting, and prospect of simultaneous recovery of other minor elements. The studies that were carried out involved: (a) calculation of phase stability in Fe_2O_3-Al_2O_3-Na_2CO_3-C system in temperature range of interest for the process, (b) evaluation of process based on experimental studies vis-à-vis phase stability results. Possible future direction of research is indicated based on the research pursued.

PHASE STABILITY IN FE_2O_3-AL_2O_3-NA_2CO_3-C SYSTEM

The calculation of thermodynamic equilibria is based on minimization of the total Gibbs free energy of the system under the constraints of elemental mass balance [6-9]. This approach was used to calculate the stability of the phases in the system Fe_2O_3-Al_2O_3-Na_2CO_3-C in the temperature range of 573-1198 K. In the Gibbs energy minimisation, the Gibbs energy of the system

$$G_{sys} = \sum_{i,\alpha} n_i^{\alpha} \mu_i^{a}, \qquad n_i^{\alpha} \geq 0 \qquad \ldots \qquad (1)$$

(where summation goes over all phases (a) and species (i) and

G_{sys} = Gibbs energy of the system

n_i = amount of species I

m_I = chemical potential of species i)

is minimized with elemental balance as a constraint

$$\sum_{i,\alpha} a_{ji} n_i^{\alpha} = b_j \quad j = 1 \ldots M, i = 1 \ldots n \qquad \ldots \qquad (2)$$

(where

M = number of elements in the system

b_j = total amount of element j in the system

a_{ji} = number of atoms j in species i)

All possible condensed phases, namely Al_2O_3, $NaAlO_2$, Fe_2O_3, Fe_3O_4, FeO, Fe, $FeAl_2O_4$, $FeNaO_2$, Na_2CO_3, C and gas phases CO, CO_2, O_2 and N_2 were considered. The thermodynamic data for the species were taken from the literature [10]. In the initial calculation, no attempt was made to include solid solution phases. The basis of the calculation was 100 g red mud [Typical composition (wt. %): Fe_2O_3 – 47.4,

Al_2O_3 - 20.4, TiO_2 - 2.82, SiO_2 - 7.4, Na_2O - 4.8, CaO - 3.2 and Loss on Ignition - 13.1]. Species other than those considered in the phase stability calculation were assumed to behave as inert phases. Thus, the fixed inputs to the programme were as follows: Fe_2O_3 - 47.4 g, Al_2O_3 - 20.4 g and Na_2CO_3 - 30.0 g. Carbon input was varied from 9 to 12 g at 1 g interval (9 g/100 g red mud is the amount used in the laboratory experiments based on literature on chemical beneficiation of aluminous iron ores [3]). The calculations were performed using a computer programme [7-10] and stability regimes for different species were determined.

The typical results of calculation, in terms of mole of significant solid species and CO/CO_2 ratio are shown in Fig. 1 and Fig. 2 for 9 and 12 g C, respectively. Fe_2O_3 is not a stable species in the range of temperature (573-1198 K) that is studied. Fe_3O_4 ® FeO and FeO ® Fe transition temperature are 779 and 1034 K, respectively. The stability of $FeAl_2O_4$ spinel phase in the system up to 1047 K is noteworthy. The reduction behaviour of $FeAl_2O_4$, and in turn complete reduction of iron, is strongly dependent on the carbon content (Fig. 1 and Fig. 2).

When the amount of carbon present is inadequate, partial reduction of $FeAl_2O_4$ in the presence of soda leads to the formation of Fe + $NaAlO_2$ in the temperature range 1047 and 1061 K accompanied with a sudden drop in the CO/CO_2 ratio. Beyond 1061 K, formation of FeO+$NaAlO_2$ takes place accompanied with an increase in CO/CO_2 ratio (Fig. 1). In sharp contrast, when the amount of C in the system is adequate, reduction of $FeAlO_2$ to Fe + $NaAlO_2$ takes place in the presence of soda at 1047 K. Also, CO/CO_2 ratio shows a continuous increase with temperature (Fig. 2). Fig. 1 and Fig. 2 establish linkages between complete reduction of iron and formation of $NaAlO_2$ phase.

EVALUATION OF THE COMPLETE CHEMICAL BENEFICIATION PROCESS

The response of a high iron Indian red mud [chemical composition (wt. %): Fe_2O_3 - 47.4, Al_2O_3 - 20.4, TiO_2 - 2.82, SiO_2 - 7.4, Na_2O - 4.8, CaO - 3.2 and Loss on Ignition - 13.1] to the process was evaluated in terms of alumina recovery during leaching, and enrichment and recovery of iron in the magnetic and non-magnetic fractions. The amount of carbon used for reduction was 9 g/100 g of red mud. Irrespective of the soda content, roasting time and leaching temperature, recovery of alumina was low (<50%) for roasting at 750 °C. SEM-EDS studies on the leach residues indicated the presence of non-reacted alumina in the form of alumina particles and complex assemblage of iron and alumina at lower roasting temperatures, i.e. 700-750 °C (Fig. 3). Increasing the roasting temperature to 925°C (beyond which the roasted mass started to fuse) could enhance the alumina recovery to 70%. At this stage the alumina in the residue corresponds to only Al-Fe bearing particles and did not contain any free alumina particles.

The summary of results on the behaviour of iron between 700-925 °C is presented in Fig. 4. X-ray phase analysis results are also superimposed in the Fig. 4 to correlate iron bearing phases formed at different temperatures with their enrichment pattern in the magnetic fraction (MF) and the non-magnetic fraction (NMF). High recovery of iron at 750 and 950 °C are attributed to formation of greater amount of magnetic oxide phase at lower temperature (magnetite/spinel phase) and metallic iron at higher temperature. Higher grade at 950 °C than that at 750 °C implies magnetic separation of magnetic iron is more effective compared to that for magnetic iron oxide. Iron in the magnetic oxide fraction is mainly present as complex phase comprising of Fe (major) along with Al and minor amount of Si [Fig 5 (a)],

whereas the metallic iron is present as rounded high purity iron globules [Fig. 5(b)]. Loss of iron with the non-magnetic fraction between 800-925 °C is primarily due to wustite and metallic iron and the presence of wustite is indicative of incomplete reduction. This corroborate the thermodynamic calculation mentioned above and explains why the alumina recovery in excess of 70% is not possible with 9% C.

FURTHER RESEARCH DIRECTIONS

Thermogravimetric studies were carried out in N_2 atmosphere on red mud samples Na_2CO_3 (1.3 times the stoichiometric requirement) and varied amount of carbon from 9 to 12 g C per 100 g red mud. Degree of reduction was calculated from a detailed analysis of the weight loss observed at 900 °C. Complete reduction was obtained in the 11 and 12% carbon samples as predicted by the thermodynamic analysis (e.g. Fig. 2) except that the temperature for complete reduction was much higher (~ 900 °C) than the thermodynamically predicted temperature (1047 K or 774 °C) possibly due to kinetics control. These results suggest bright prospect of developing a chemical beneficiation process through appropriate selection of reduction conditions.

MECHANOCHEMICAL ACTIVATION OF BAUXITE AND ALKALI LEACHING

Recently, there has been a spurt of research activities in the applications of mechanical activation for the development of new materials and eco-friendly metallurgical processes for oxide/hydroxide and sulphide ores, waste materials etc [11-13]. Mechanical activation (more appropriately mechanochemical activation) of bauxite as well as red mud, that involves solid state reactions in high energy milling devices, has attracted the attention of researchers in Germany, China, Australia, and more recently, India (at NML). The basic idea of research pursued at NML has been to achieve moderation in process conditions, reduce alumina and soda losses in the red mud, etc [11-13].

MECHANICAL ACTIVATION AS PRE-TREATMENT AND MECHANOCHEMICAL LEACHING

Effect of mechanical activation of bauxite was investigated as pre-treatment, that is separate milling and leaching (SEMIL). In order to exploit short-lived mechanochemical effect, simultaneous milling and leaching (SMILE) experiments were also carried out. The results for chemical leaching, SEMIL and SMILE along with typical plant data for the same bauxite are compared in Table 1. Beneficial effect of mechanical activation is quite evident from the results. Mechanical activation results in complete elimination of gibbsite phase from the leach residue. SMILE and SEMIL resulted in comparable alumina recovery at 90 °C under identical condition. However, greater soda loss was observed in SEMIL highlighting the importance of coupling mechanical activation with the leaching process. The concept of SMILE is also superior to SEMIL in terms of leaching time, 15 min and 90 min respectively, energy utilisation and simplicity of operation

Table 1: Comparison of results of chemical leaching, SEMIL and SMILE with Plant data

Leaching process	Operating parameters			Al_2O_3 recovery, %	Na_2O in red mud, %
	Na_2O g/l	Time, min	Temperature °C		
Chemical	180	75	90	67.6	0.81
	180	75	106	89.5	2.14
With MA					
SEMIL	180	90	90	89.6	0.90
	180	90	106	91.5	2.33
SMILE	180	15	90	89	0.68
Typical plant	180	300	106	85-87	3-4

NATURE OF LEACH RESIDUE

The mineral gibbsite was completely eliminated in the leach residue obtained after mechanochemical leaching. After mechanical activation of bauxite, hematite was the dominant mineral in the leach residue, and not gibbsite and hematite as observed in the plant red mud. Kaolinite was present in the leach residue of mechanically activated bauxite and sodalite present in the plant red mud was absent.

UNRESOLVED ISSUES

The results presented indicate that mechanical activation of bauxite results in the improved alumina recovery. The higher recovery is possible at lower temperature and much reduced duration of leaching. The soda content of the red mud is reduced significantly in the experiments involving simultaneous milling and leaching. A number of unresolved issues remains, for example the nature of Al-bearing phases in the laboratory red mud, the opportunity for further improvement in alumina recovery, and the understanding of the lower soda content of red mud in larger scale experiments. The possibility of the conversion of goethite into hematite under milling condition and the settling behaviour of red mud are other issues that also require further study.

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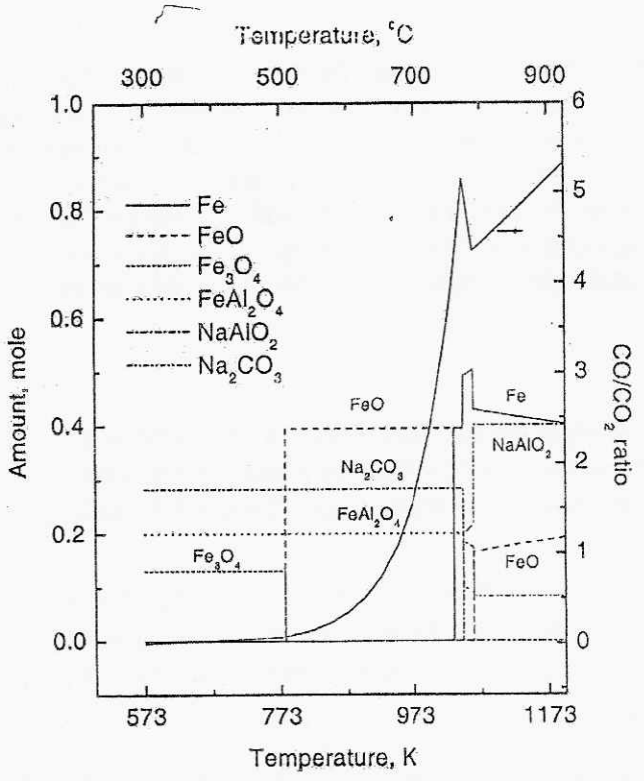


Fig. 1 Stability of phases in the Al_2O_3-Fe_2O_3-Na_2CO_3-C system as determined using free energy minimisation with following inputs (in g): Fe_2O_3-47.4, Al_2O_3-20.4, Na_2CO_3-30, C-9

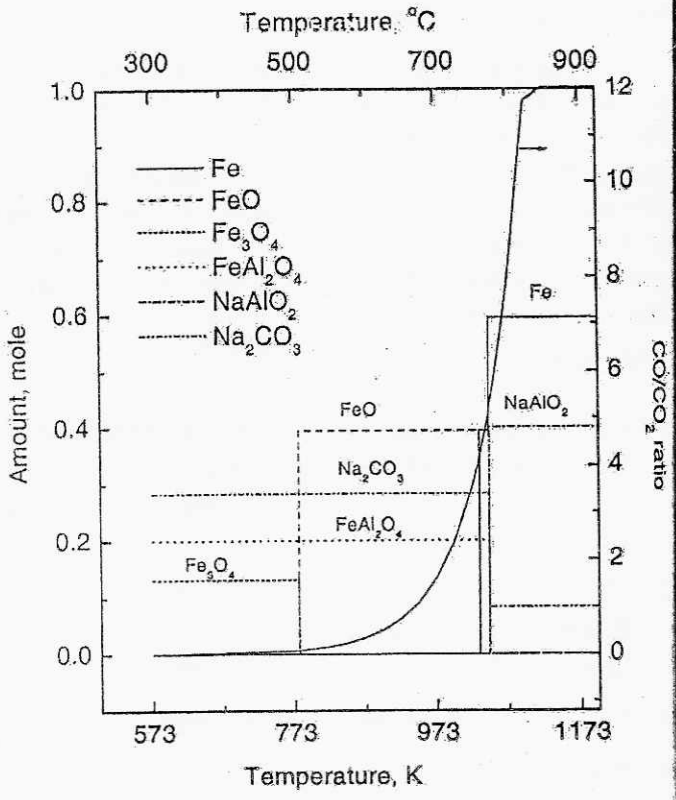


Fig. 2 Stability of phases in the Al_2O_3-Fe_2O_3-Na_2CO_3-C system as determined using free energy minimisation with following inputs (in g): Fe_2O_3-47.4, Al_2O_3-20.4, Na_2CO_3-30, C-12

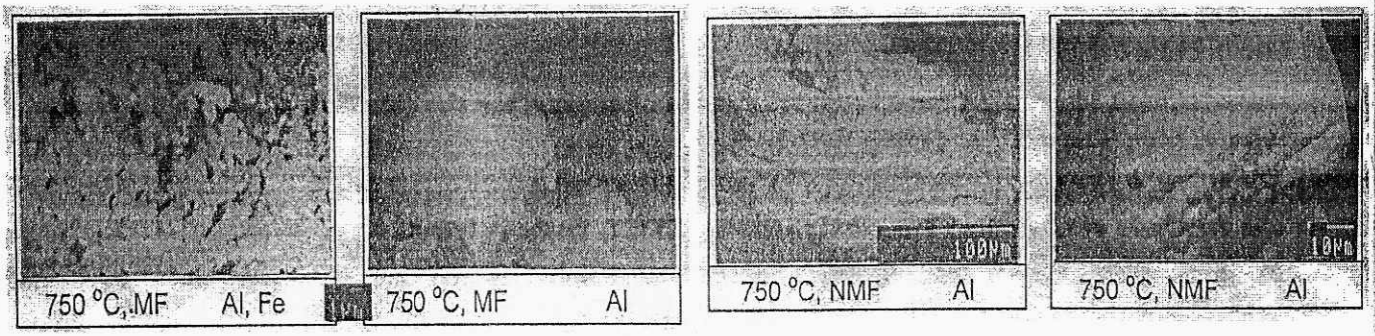


Fig. 3 SEM micrographs of non-reacted aluminium bearing particles in the leach residue obtained after leaching (Elemental composition obtained by EDS analysis).

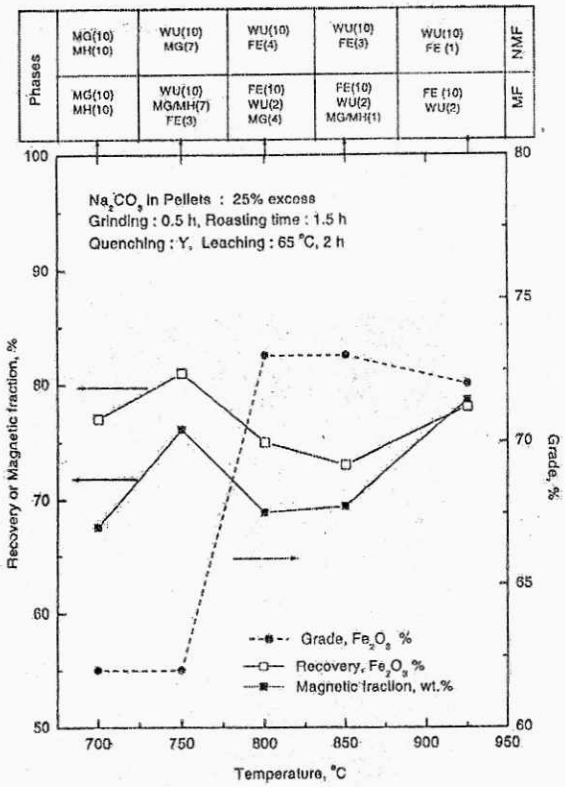
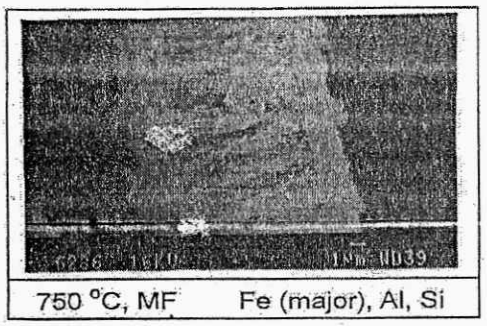


Fig. 4 Effect of roasting temperature on the behaviour of iron during magnetic separation. Phases separated in the magnetic fraction (MF) and nonmagnetic fraction (NMF) for different roasting temperatures are indicated along with the relative intensity.
MH-Maghemite, MG-Magnetite, WU-Wustite



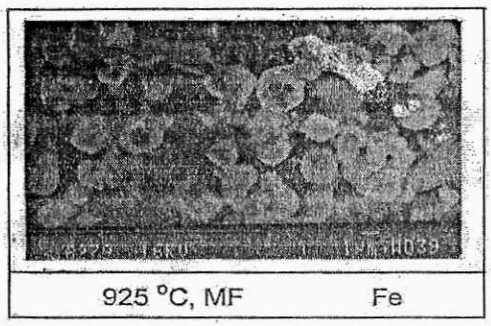


Fig. 5 SEM photomicrographs of iron bearing particles obtained at different roasting temperatures: (a) iron present as oxide in magnetic fraction, roasting temperature 750 °C; and (b) metallic iron as rounded globules, roasting temperature 925 °C